

RESEARCH PAPER RP796

Part of Journal of Research of the National Bureau of Standards, Volume 14,
June 1935

AN APPARATUS FOR MEASURING THE BOILING POINTS OF LUBRICATING OILS AND OTHER COMPOUNDS OF HIGH MOLECULAR WEIGHT AT REDUCED PRESSURES ¹

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ABSTRACT

This paper describes an apparatus suitable for determining accurately the boiling points of lubricating oils and other compounds of high molecular weight at temperatures and pressures below their decomposition points. The temperatures are determined by means of three thermocouples located at different heights in the vapor column, which, by their differences in temperature, give some indication of the purity of the sample, the readings of the three thermocouples being identical for a pure substance. The pressures are determined with a McLeod gage.

Data are reported for pure di-*n*-butyl phthalate, for mixtures of di-*n*-butyl phthalate with 6.82, 10.62, and 18.75 mole percent of trio-*o*-cresyl phosphate, and for two lubricating-oil fractions obtained from successive distillations.

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I. INTRODUCTION

In the distillation of complex liquid mixtures at very low external pressures (<0.001 mm of Hg), it has been shown by Hickman ³ that the temperatures usually obtained in the distilling zone are not truly related to the pressure determined by a gage in the external part of the system, because of the unknown variable drop in pressure between these two points. For the proper reblending of cuts during systematic separation, it is necessary to know the boiling points of the various fractions, and for this reason it was desirable to construct an apparatus that would indicate the true boiling points at a given pressure. This apparatus should be easy to clean, manipulate, and recharge, accurate to within 1° C, permit rapid measurements, and have its operating range below the decomposition temperature of the substances to be studied.

¹ Financial assistance for this work has been received from the research fund of the American Petroleum Institute. This work is part of Project 6, The Separation, Identification, and Determination of the Constituents of Petroleum.

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³ K. Hickman and W. Weyerts, J. Am. Chem. Soc. **52**, 4714 (1930).

This paper describes such a boiling-point apparatus, and gives experimental data showing the applicability of the apparatus to the problem of determining the boiling points of lubricating-oil fractions and other high-boiling compounds at various pressures below the point of decomposition.

II. DESCRIPTION OF APPARATUS

Figure 1 shows schematically the boiling-point apparatus and its necessary accessories. E is the boiling-point tube, which contains a ground-glass joint B' for the filling and cleaning of the apparatus, and G is an all-glass internal stirring mechanism.⁴ Tube E is made about 30 mm in diameter so that the drop in pressure between the top and bottom during a determination is negligible. The tube is vacuum-jacketed above the heater unit in order to minimize, as far as possible, any heat leak from the ascending vapors.

The lower part of the tube E fits into an insulated box H, which contains the heater I and the magnets F. The magnets F are placed symmetrically around the upper part of the stirrer and in a direct line with the upper arm, which is constructed of an iron core inclosed in glass. The upper portion of the tube is connected, by means of all-glass seals, to a ballast tank B (3-liter capacity), bulb P (of 2-liter capacity and filled with dry pure nitrogen), the trap O, McLeod gage U', and to the mercury-vapor pump through the stopcock Q.

The temperatures in the vapor column are determined by three thermocouples, C, constructed of copper wire (no. 36 AWG gage) and constantan wire (no. 32 AWG gage), and placed at various heights in the tube. The thermocouples are held in the central portion of the apparatus by means of a perforated glass tube D, which allows the hot vapors to pass freely around the thermoelements. About 1 inch of the wires is coiled about the copper-constantan tip in order to secure thermal equilibrium at the junction. The thermocouples are sealed into the apparatus at A by means of hard de Khotinsky cement.

The top view of the transite block holding the magnets in place, around the boiling-point tube, is shown at E' with a schematic electrical connection to the actuating commutator. The commutator X is made of bakelite board, on which is mounted a discontinuous brass ring V. Each segment of the ring is wired to a magnet. The magnets are consecutively activated by means of the rotor W, consisting of a brass tube making contact with the brass ring by means of carbon brushes, and being rotated by means of a variable-speed motor Y.

Bulb P containing pure dry nitrogen is connected to the system by means of a 3-way stopcock. The amount of gas released into the system is measured approximately by the bulb N (volume 0.5 ml), which is a sealed-off arm of the stopcock.

The McLeod gage U', constructed so that pressures between 0.001 and 4.840 mm of Hg can be measured with an accuracy of $\pm .001$ mm of Hg, is connected to the system through the trap O, which keeps the condensable vapors from entering the gage. The central tube S of the gage is graduated in millimeters and numbered from the top to the bottom. In the outer capillary tube S' are sealed two tungsten points R and U, which are connected to the galvanometer T. This arrange-

⁴ Designed by Francis A. Smith and G. Martin Shepherd of the National Bureau of Standards.

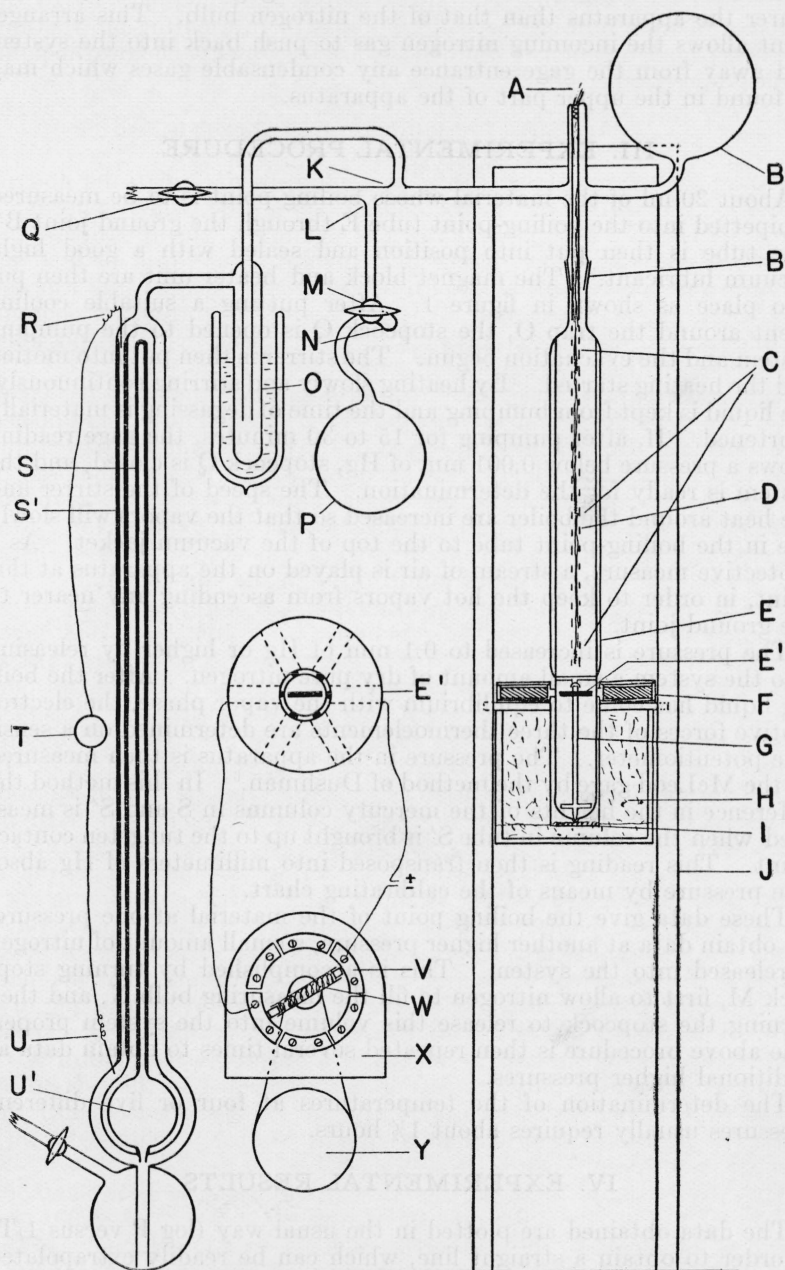


FIGURE 1.—Boiling-point apparatus for use at reduced pressures.

[Explanatory diagram]

ment is used in order to raise the mercury column to the same height at all times. The entrance of the McLeod gage into the system is nearer the apparatus than that of the nitrogen bulb. This arrangement allows the incoming nitrogen gas to push back into the system and away from the gage entrance any condensable gases which may be found in the upper part of the apparatus.

III. EXPERIMENTAL PROCEDURE

About 20 ml of the material whose boiling point is to be measured is pipetted into the boiling-point tube E through the ground joint B'. The tube is then put into position and sealed with a good high-vacuum lubricant.⁵ The magnet block and heater unit are then put into place as shown in figure 1. After putting a suitable cooling agent around the trap O, the stopcock Q is opened to the pumping system and the evacuation begun. The stirrer is then put into motion and the heating started. By heating slowly and stirring continuously, the liquid is kept from bumping and the time of degassing is materially shortened. If, after pumping for 15 to 30 minutes, the gage reading shows a pressure below 0.001 mm of Hg, stopcock Q is closed, and the system is ready for the determination. The speed of the stirrer and the heat around the boiler are increased so that the vapors will slowly rise in the boiling-point tube to the top of the vacuum jacket. As a protective measure, a stream of air is played on the apparatus at this point, in order to keep the hot vapors from ascending any nearer to the ground joint.

The pressure is increased to 0.1 mm of Hg or higher by releasing into the system a small amount of dry pure nitrogen. After the boiling liquid has come to equilibrium with the vapor phase, the electromotive forces of the three thermoelements are determined on a sensitive potentiometer. The pressure in the apparatus is then measured on the McLeod gage by the method of Dushman.⁶ In this method the difference in the heights of the mercury columns in S and S' is measured when the column in tube S' is brought up to the tungsten contact point. This reading is then transposed into millimeters of Hg absolute pressure by means of the calibrating chart.

These data give the boiling point of the material at one pressure. To obtain data at another higher pressure, a small amount of nitrogen is released into the system. This is accomplished by turning stopcock M, first to allow nitrogen to fill the measuring bulb N, and then turning the stopcock to release this volume into the system proper. The above procedure is then repeated several times to obtain data at additional higher pressures.

The determination of the temperatures at four or five different pressures usually requires about 1½ hours.

IV. EXPERIMENTAL RESULTS

The data obtained are plotted in the usual way ($\log P$ versus $1/T$) in order to obtain a straight line, which can be readily extrapolated over a short range without significant error. In this way, the boiling points of all the substances can be obtained at some predetermined pressure. However, data obtained with the apparatus at pressures

⁵ T. P. Sager, *Ind. Eng. Chem., Anal. Ed.* **4**, 388 (1932).

⁶ Saul Dushman, *Gen. Elec. Rev.* **23**, 731 (1920).

below 0.1 mm of Hg deviate considerably from the linear relation, and consequently the working range was limited to pressures between 0.1 and 4.8 mm of Hg. Hickman⁷ also found this deviation at low pressures.

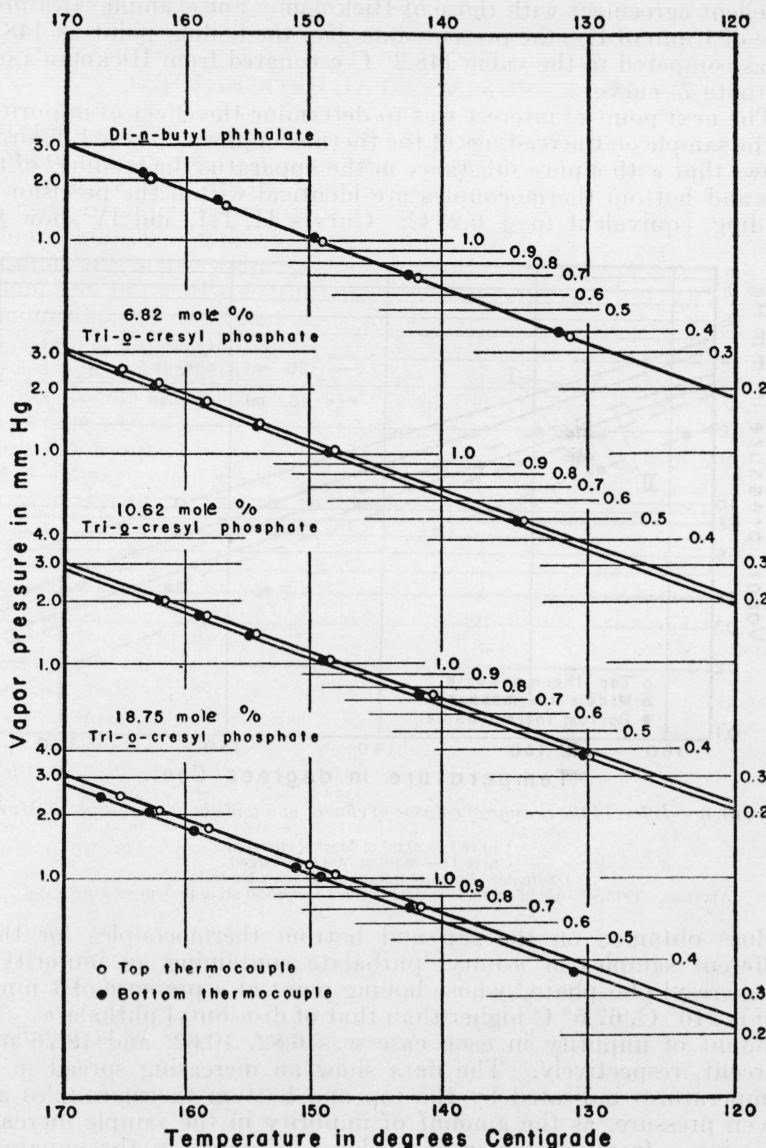


FIGURE 2.—Variation of the readings of the top and bottom thermocouples as the amount of impurity (tri-o-cresyl phosphate) in di-n-butyl phthalate is increased.

Ordinate.—Pressure in mm of Hg (on a log scale).

Abscissa.—Temperature in degrees Centigrade (on a reciprocal absolute-temperature scale).

To check the accuracy of the values of vapor pressure determined in this apparatus, data were first obtained on pure di-n-butyl phthal-

⁷ K. C. D. Hickman, J. Phys. Chem. **34**, 629 (1930).

ate, whose vapor pressure-temperature relations had been accurately measured by Hickman (see footnote 7) with a different kind of apparatus. Curve I, figure 2, shows the data obtained on di-*n*-butyl phthalate. The values obtained with the present apparatus are in excellent agreement with those of Hickman. For example, at a pressure of 1 mm of Hg, the present data give the boiling point as 148.5° C, as compared to the value 148.2° C estimated from Hickman's (see footnote 7) curve.

The next point of interest was to determine the effect of impurities in the sample on the readings of the thermocouples. Curve I, figure 2, shows that with a pure substance in the apparatus the readings of the top and bottom thermocouples are identical within the precision of reading, equivalent to $\pm 0.2^\circ\text{C}$. Curves II, III, and IV show the

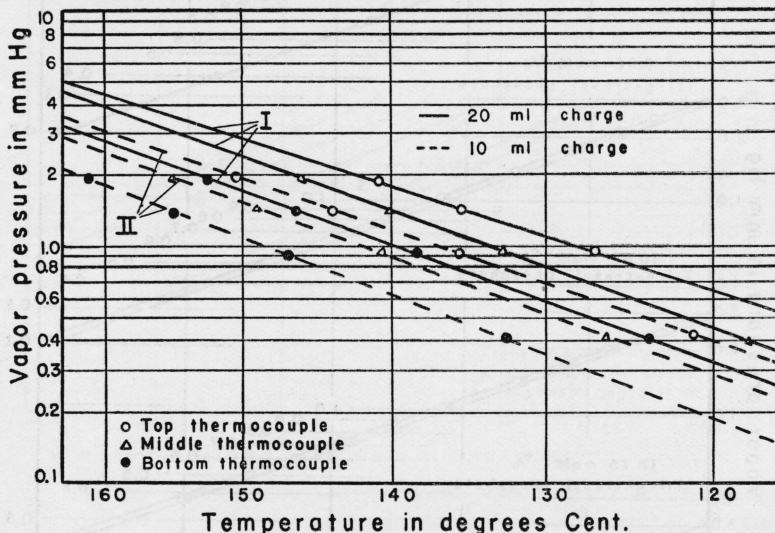


FIGURE 3.—Effect of the change of volume of charge of a wide-boiling sample of Markol.

Curve I.—20 ml of Markol charged.

Curve II.—10 ml of Markol charged.

Ordinate.—Pressure in mm of Hg (on a log scale)

Abscissa.—Temperature in degrees centigrade (on a reciprocal absolute-temperature scale).

values obtained on the top and bottom thermocouples for three different samples of *n*-butyl phthalate containing an impurity of tri-*o*-cresyl phosphate,⁸ whose boiling point at a pressure of 1 mm of Hg is 216° C, 67.5° C higher than that of di-*n*-butyl phthalate. The amount of impurity in each case was 6.82, 10.62, and 18.75 mole percent, respectively. The data show an increasing spread in the temperatures indicated by the top and bottom thermocouples at a given pressure, as the amount of impurity in the sample increases, showing a fractionation in the column of vapor in the apparatus. No spread in the readings would be expected if the impurity had, at a given pressure, the same boiling point as the solvent. In obtaining the above-mentioned data the same volume of sample, 16 ml, was used in each case.

⁸ Obtained from M. R. Fenske, Pennsylvania State College.

It was next desirable to determine whether the data obtained varied with the volume of liquid in the apparatus. For a pure substance, di-*n*-butyl phthalate, the values obtained with a sample of 10 ml were identical, within the accuracy of the readings, with the values obtained with a sample of 20 ml. For an impure substance, however, this would not be expected, because, with the vapor space filled, the composition of the liquid in the two cases would be different. This excludes the case where the impurity has the same vapor pressure as the solvent. In figure 3 are given the data obtained on a sample of "Markol", a lubricating oil having a wide boiling range. The

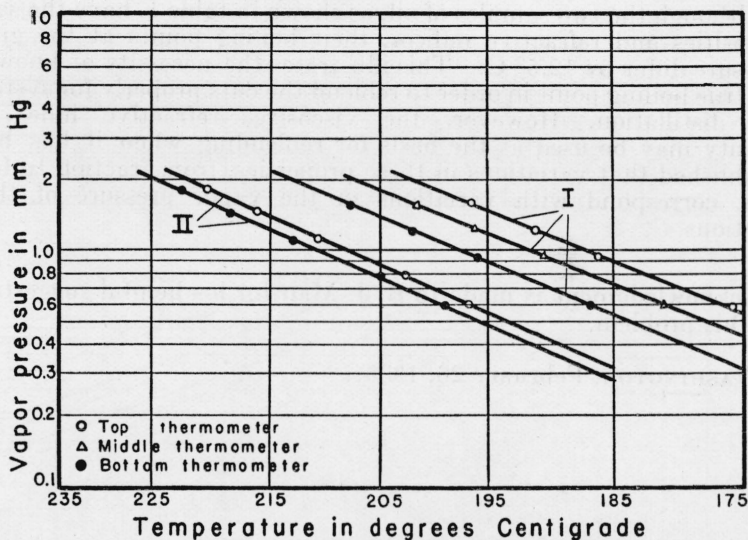


FIGURE 4.—Effect of a distillation on a lubricating-oil sample.

Curve I.—Original oil.

Curve II.—Middle fraction after distillation of original oil.

Ordinate.—Pressure in mm of Hg (on a log scale)

Abscissa.—Temperature in degrees centigrade (on a reciprocal absolute temperature scale).

two sets of curves indicate the change in reading as the volume of sample is changed from 10 to 20 ml.

It was also found that the data obtained for a given sample did not change with the rate of heat input into the boiler if the sample was pure, but did change somewhat (of the order of 1°C for a 7 per cent increase in the heat input) if the sample was not pure.

In figure 4 are plotted the data obtained on two cuts from successive fractional distillations of lubricating oil. Curve I gives the data on the initial water-white lubricating oil and curve II on one of the middle cuts from the first distillation in a laboratory still. The boiling-point data on these two samples, together with their refractive indices, viscosities at 100 and 210°F , and history are given in table 1.

TABLE 1.—*Relation of the boiling point to other physical properties of two lubricating-oil samples*

Curve (fig. 4)	Viscosity, in Saybolt seconds, at—		Refractive index at 25° C	Boiling point at 1 mm Hg at ° C	History of material
	100° F	210° F			
I.....	156.9	43.8	1.4733	198	Original water-white lubricating oil. 10th (middle) fraction obtained from the distillation of the above fraction.
II.....	156.7	43.4	1.4733	210.5	

Although the two samples of oil, as shown in table 1, have the same viscosities and refractive indices, their boiling points at the given pressure differ by 12.5° C. This illustrates the necessity of knowing the true boiling point in order to reblend the cuts properly for systematic distillation. However, the viscosity, refractive index, or density may be used as the basis for reblending when it has been established that variations in these properties, from fraction to fraction, correspond with variations in the vapor pressure of these fractions.

Acknowledgment is made to B. J. Mair for his helpful suggestions on this problem.

WASHINGTON, February 26, 1935.